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Effect of Physical Annealing on the Dynamic Mechanical
Properties of A High T_g Amine-Cured Epoxy System

by

G. Wisanrakkit and J. K. Gillham

Polymer Materials Program
Department of Chemical Engineering
Princeton University
Princeton, NJ 08544

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Principal Investigator
John K. Gillham
(609) 452-4694

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MECHANICAL PROPERTIES OF A HIGH T_g
AMINE-CURED EPOXY SYSTEM**

BY

GUY WISANRAKKIT and JOHN K. GILLHAM

**POLYMER MATERIALS PROGRAM
DEPARTMENT OF CHEMICAL ENGINEERING
PRINCETON UNIVERSITY
PRINCETON, NJ 08544**

ABSTRACT

Physical annealing of a fully cured epoxy system ($T_{g\infty}=180^\circ\text{C}$) has been investigated using the torsional braid analysis (TBA) technique. The dynamic mechanical properties were monitored during isothermal annealing at sub- T_g temperatures (-30 to 150°C). The properties after annealing were measured vs. temperature and compared with those of the unannealed state. Isothermally, the relative rigidity increased linearly with log time, whereas the logarithmic decrement decreased with time. Temperature-scanning the isothermally annealed material showed a maximum deviation from the unannealed material in the vicinity of the annealing temperature. Effects of sequential annealing at different isothermal temperatures suggested that annealing at different temperatures involves different scales of chain segment relaxation.

INTRODUCTION

Studies on high T_g amine-cured epoxy systems show that the room temperature (RT) modulus as well as the RT density decrease with increasing extent of cure (i.e., T_g) [1-3]. For example, Figure 1 shows the phenomenon in terms of sequential dynamic mechanical TBA temperature scans of a partially and the fully cured specimen. Note that the relative rigidity (\sim shear modulus) at RT of the undercured specimen (i.e. with low T_g) is higher than that of the fully cured specimen [See caption to Fig. 1]. An explanation has been proposed which attributes the increasing free volume in the glassy state at RT to the non-linear increase of T_g with conversion [3]. An alternative explanation depends on the efficiency of densification in the T_g region being higher for low T_g material [3]. The present study deals with the annealing behavior of fully cured specimens as a background for studies on undercured materials.

Recent preliminary annealing studies on an epoxy system using the TBA technique have shown that sub- T_g annealing of high T_g epoxies affects thermomechanical properties principally in the vicinity of the annealing temperature, and in particular, annealing at temperatures well above RT does not significantly affect the RT density and mechanical properties [4]. The TBA technique can be a useful and sensitive way for monitoring the physical annealing process over a wide temperature range through the changes in the mechanical properties which are closely related to the specific volume of the material. The effect of isothermal annealing on material behavior is made apparent by comparing temperature scans of isothermally annealed specimens with those of unaged material. A glass braid supporting the material permits erasure of prior annealing effects by taking the material to above its T_g so that many experiments can be performed using one specimen.

Results of an annealing study on a fully reacted amine-cured epoxy system using the TBA technique are presented here. The dynamic mechanical properties of the material are monitored during isothermal annealing at different temperatures. The properties vs. temperature after annealing are compared with those of the unannealed state. Effects of a sequential annealing at two different isothermal temperatures are also examined.

EXPERIMENTAL PROCEDURE

The chemical system used was a neat mixture of a difunctional epoxy and a

tetrafunctional aromatic diamine in a stoichiometric ratio (Fig.2).

A TBA specimen was made by impregnating a heat-cleaned glass braid with the solution of the reactants. The specimen was cured in the TBA at 200°C for 75 hr. This temperature was chosen because (a) the material could be fully reacted in the absence of vitrification (since T_g of the fully cured system = 180°C), (b) the specimen would be heated to 200°C after subsequent annealing experiments to eliminate the prehistories, and (c) no degradation was observed at 200°C. After the isothermal cure, the specimen was taken through the temperature scan: 200→-180→200°C at 1°C/min. during which the relative rigidity and logarithmic decrement of the unannealed material were obtained. Repeated cooling from and heating to 200°C at the same rate did not affect the thermomechanical spectra. All curing and subsequent experiments were performed under a flowing dry helium atmosphere.

Annealing Procedure: The "fully reacted" specimen was taken to 200°C and then cooled at 5°C/min to a prespecified annealing temperature (T_a) below T_g . The material was allowed to anneal isothermally at T_a , while its relative rigidity and logarithmic decrement were continuously monitored for exactly 10,000 min (except for $T_a = -30^\circ\text{C}$ for which the time of annealing was 600 min). The temperature was maintained at T_a to within $\pm 0.1^\circ\text{C}$ (after the initial transient period of approximately 20 minutes). The specimen was then cooled from T_a to -180°C and then heated to 200°C to obtain the properties of the annealed material as a function of temperature. Subsequent cooling from 200°C to -180°C provided thermomechanical spectra of the material, which were compared with those of the unannealed material obtained immediately after curing. This provided an internal means of checking for irreversible changes. Annealing was performed at different temperatures (ranging from -30 to 150°C). For each experiment, the specimen was heated to 200°C to erase the previous annealing histories (see later), and cooled to the new T_a at 5°C/min. In principle, one specimen could have been used for all the experiments.

Effects of sequential isothermal annealing at two different temperatures were also examined. The specimen was annealed at the first temperature (T_{a1}) for 10,000 min., and then, after changing to a new annealing temperature (T_{a2}) at 5°C/min., the specimen was allowed to anneal at T_{a2} for 10,000 min. The specimen was then subjected to temperature scan: $T_{a2} \rightarrow -180 \rightarrow 200 \rightarrow -180^\circ\text{C}$ at 1°C/min, so as to obtain the behavior of the material vs. temperature. In one set of experiments $T_{a1} > T_{a2}$; in another set $T_{a1} < T_{a2}$.

RESULTS AND DISCUSSION

I. Mechanical Spectra of the Fully Cured Specimen.

Figure 3 shows the dynamic mechanical properties vs. temperature of the specimen after curing at 200°C for 75 hr. The solid lines represent the behavior measured during scanning from 200°C to -180°C and the dotted lines denote the behavior on subsequent scanning from -180°C to 200°C. The T_g of the material is 180°C. The secondary (β) transition is centered around -30°C. It is noted that the spectra on cooling differ from those on heating in the glass transition below T_g . This can be attributed to the temperature scan rate at 1°C/min being slow enough to allow the material to anneal to a small extent during cooling and subsequent heating.

II. Reversibility of the Physical Annealing Phenomenon.

Figure 4 shows the mechanical spectra of the specimen which has previously been annealed at 100°C for 10,000 min. and heated to 200°C, measured during a

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temperature scan from 200°C (dotted curves), compared with the spectra of the same specimen from 200°C prior to annealing experiment (solid curves). The spectra of the annealed material coincide with those of the unannealed material completely. This indicates that thermal annealing histories in the glassy state can be erased by heating the material to above its T_g and that no irreversible changes occur during isothermal annealing and subsequent heating to 200°C and cooling. Therefore, the initial state of the material prior to physical annealing can be reproduced by simply heating the material 20°C above its T_g . Consequently, annealing behavior at different temperatures can be examined on a single specimen.

III. Isothermal Annealing Behavior

The level of the initial relative rigidity of an unannealed specimen decreases monotonically with increasing temperature. During isothermal annealing, the rigidity of the specimen increases with annealing time, while the logarithmic decrement decreases with time. Figures 5A and 5B show the annealing results at four different annealing temperatures (150, 60, 30 and -30°C) for one specimen. Note that the scale in Figures 5A and 5B has been expanded more than 100 times over that for Figure 6. The results demonstrate the nonequilibrium nature of the material even at temperatures far below T_g (30-210°C below T_g). For all of the annealing temperatures, the material is still changing at the end of the 10,000 min (600 min for $T_a = -30^\circ\text{C}$). Theoretically, the material will eventually reach its equilibrium state and the changes would level off after prolonged annealing times. At annealing temperatures close to T_g , the equilibrium state can be achieved faster since the relaxation time is much shorter and the material is closer to equilibrium [4,5].

Since the rigidity is related to the specific volume of the material, the rate of physical annealing (volume relaxation) can be measured from the rate of change of the rigidity. The rate of annealing (from the rigidity curves in Fig. 5A) appears to increase only slightly with increasing annealing temperature. Isothermally, after approximately 100 minutes, the rigidity, R , increases almost linearly with the logarithm of annealing time, t : $R = A_T + B_T \log_{10} t$ (A_T and B_T are constants for each T_a). The rate of annealing is, therefore, $r_a = dR/dt = 2.303B_T/t$. Thus, the rate of annealing decreases inversely with the annealing time.

IV. Dynamic Mechanical Properties vs. Temperature of Annealed Specimen

The TBA spectra vs. temperature obtained during the temperature scan: $T_a \rightarrow 180 \rightarrow 200 \rightarrow -180^\circ\text{C}$ at $1^\circ\text{C}/\text{min}$ of a specimen after annealing at different temperatures are summarized in Figures 6A and 6B, respectively. The results of the temperature sequence: $T_a \rightarrow -180 \rightarrow 200^\circ\text{C}$ are shown as dotted lines; spectra of the same specimen cooled from 200°C to -180°C, taken as the unannealed state, are shown as solid lines for comparison.

The differences between spectra of the annealed and the unannealed specimen are found to be most pronounced in the vicinity of the annealing temperatures, in which the mechanical behavior of the former (higher rigidity and lower logarithmic decrement) deviates most from the latter. Below the vicinity of the annealing temperature, the physical annealing does not seem to significantly affect the mechanical spectra of the material. However, on expanding the scales, the results reveal small but definite differences throughout the entire temperature range of the glassy state as shown in Figure 7.

For the specimen which has been annealed at low temperatures (e.g. $T_a = 30^\circ\text{C}$ and 60°C), the rigidity is found to be slightly lower than the unannealed value in the temperature range approximately 40°C above T_a to below T_g , while the

corresponding logarithmic decrement in this temperature range is noticeably higher. A plausible molecular description for this observation is as follows. The annealed glass has a longer relaxation times due to decreasing free volume on annealing [6,7]. On heating above the annealing temperature, the longer relaxation time causes the annealed state (higher rigidity) to persist beyond the annealing temperature. On further heating to higher temperatures (approximately 30-40°C above T_a), the annealed glass relaxes and the free volume increases which causes the rigidity of the material to decrease to the value of the unannealed state or lower if the material overrelaxes in a short period of time.

Another issue on sub- T_g annealing studies concerns the effects of physical annealing on the secondary transition (T_β). There have been reports that physical annealing does not significantly affect T_β [8,9] while some reports suggest otherwise [10,11]. Our results at high annealing temperatures (e.g. 100, 120, and 150°C) show that annealing at these temperatures does not significantly affect T_β . However, the annealing results at low temperatures close to T_β (e.g. 60, 30 and -30°C) show that the secondary relaxation can be substantially influenced by physical aging in the vicinity of T_β . For example, annealing results at -30°C can also produce a higher rigidity and lower logarithmic decrement in the vicinity of the secondary transition.

Physical aging does not affect the location of the maximum of the T_g peak in the logarithmic decrement spectra, which is identified as the operational glass transition temperature, T_g , of the system. The annealing histories have virtually been erased when the temperature reaches the assigned value of T_g . Thus, by this particular way of defining T_g , the physical annealing does not change the temperature assigned to T_g .

V. Effects of Sequential Isothermal Annealing

The results of the isothermal annealing at a temperature below T_g show that there is a range of maximum perturbation in the vicinity of the annealing temperature in the thermomechanical spectra of the annealed material as compared to the unannealed state. Therefore, it is of interest to examine the effects of sequential isothermal annealing at different temperatures on the perturbation behavior.

Four sets of experiments have been carried out. The annealing time and temperatures for each set of the experiments are given in Table 1.

Experiment	T_{a1}/t_1	T_{a2}/t_2
1	120°C/10,000 min	60°C/10,000 min
2	60°C/10,000 min	120°C/10,000 min
3	60°C/10,000 min	30°C/10,000 min
4	30°C/10,000 min	60°C/10,000 min

In experiments 1 and 3, the first annealing temperatures are higher than the second temperatures, whereas in experiments 2 and 4, the reverse temperature sequences are followed. The heating and cooling rates from T_{a1} to T_{a2} are 5°C/min. After each experiment, the rigidity and the logarithmic decrement vs. temperature of the specimen were obtained during a temperature scan: $T_{a2} \rightarrow -180 \rightarrow 200 \rightarrow -180^\circ\text{C}$ at 1°C/min (Figs. 8A, 8B).

For experiments 1 and 3, in which $T_{a1} > T_{a2}$, the resulting thermomechanical spectra seem to be a combination of the separate annealing at T_{a1} and T_{a2} . The regions of maximum perturbation from the unannealed state appear in the vicinities of both T_{a1} and T_{a2} . In experiments 2 and 4, the specimen was heated to a higher

second annealing temperature. The mechanical spectra after the successive annealing only reflect the characteristics of the second annealing temperature with the region of maximum perturbation only in the vicinity of T_{a2} .

These results suggest that physical annealing at different temperatures involves different scales of relaxations. An annealed state attained at a higher temperature is unaffected by subsequent annealing at a lower temperature, which may only involve relaxations of chain segments and free volume of smaller scales. On the other hand, the annealing effects at low temperature can be erased (by increasing free volume and shortening relaxation times) when the temperature is raised to a higher temperature. Subsequent annealing at the higher temperature involves the relaxation of longer chain segments (and therefore larger scale volumes) which include those of smaller scale. Consequently, the net result of the combined annealing when $T_{a2} > T_{a1}$ is as though the material has only been annealed at the second temperature.

CONCLUSIONS

Technique: 1) The torsional braid analysis technique (TBA) is a convenient and sensitive method for monitoring the physical annealing process for the following reasons: (a) The changes in the dynamic mechanical properties are closely related to the changes in the specific volume of the materials. The changes of the former can be several orders of magnitude greater than those of the latter, and thus, can be monitored more easily. (b) The time-dependent changes in the dynamic mechanical properties of the material due to physical annealing can be monitored at isothermal annealing temperatures and, using the same unperturbed specimen, effects of the time and temperature of annealing prehistories can be examined as a function of temperature over a wide temperature range.

2) Prior annealing prehistories can be erased by taking the material to above its T_g . (i.e. physical annealing is a thermoreversible process.)

3) The sensitivity of the freely-vibrating freely-suspended specimen is revealed by comparing the isothermal annealing data with scale expansion >100 times (e.g. Figs. 5A and 5B), with that of a conventional presentation (e.g. Fig. 6).

Results: 4) During prolonged annealing, the relative rigidity increases linearly with log time, while the logarithmic decrement decreases with time. The rate of annealing is found to decrease inversely with time. The rate vs. temperature of annealing does not change drastically with temperature.

5) Temperature scans of the annealed material show that its thermomechanical spectra deviate most pronouncedly from those of the unannealed state in the vicinity of the annealing temperatures.

6) The specimen which has been annealed at one temperature and subsequently annealed at a lower temperature displays the annealing effects of both temperatures, i.e. the thermomechanical spectra show regions of maximum perturbation in the vicinities of both annealing temperatures. If the sequence of the annealing temperatures is reversed, (i.e. first annealing at a low temperature, then at a high temperature), the net result only reflects the annealing effects of the higher temperature. These results suggest that different scales of relaxation are associated with different annealing temperatures.

7) It remains to be proven that it is changes in the epoxy which produce the observed phenomenon and not the composite nature of the specimen (impregnated glass braid). This subject is under current investigation using neat epoxy films.

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FIGURE CAPTIONS

Fig. 1: Dynamic mechanical properties vs. temperature: (1A) relative rigidity, (1B) logarithmic decrement. Curves a and b are for a specimen partially cured at (160°C for 2hr.). Curves c and d are for the fully cured specimen. The sequential TBA temperature scans at 1°C/min are: (a) 160→-180°C, (b) -180→250°C, (c) 250→-180°C, and (d) -180→250°C. (Data above 200°C not shown)

Notes: (1) The T_g of the partially cured specimen increases during heating to 250°C due to additional chemical reaction. (2) The RT relative rigidity of the undercured specimen is higher than that of the fully cured specimen. For a specimen which is vitrified ($T_g \geq T_{cure}$) during the isothermal cure, sub- T_g annealing at the cure temperature could also occur and could contribute to the increase in RT rigidity [3]. However, in this example, the undercured specimen did not vitrify during the isothermal cure; therefore, physical annealing did not occur during cure. (3) The relative rigidity of the fully cured specimen becomes slightly higher than that of the undercured specimen below 0°C. This is attributed to the shift in the secondary transition to a higher temperature for the fully cured specimen (Fig. 1B), which causes its relative rigidity to cross that of the undercured specimen.

Fig. 2: Chemical reactants.

Fig. 3: TBA behavior vs. temperature of the fully cured specimen (200→-180→200°C at 1°C/min)

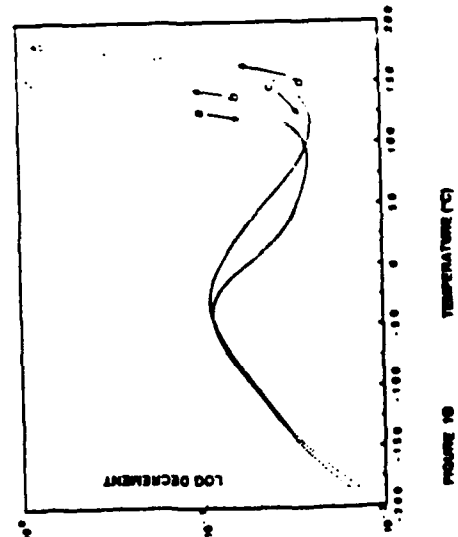
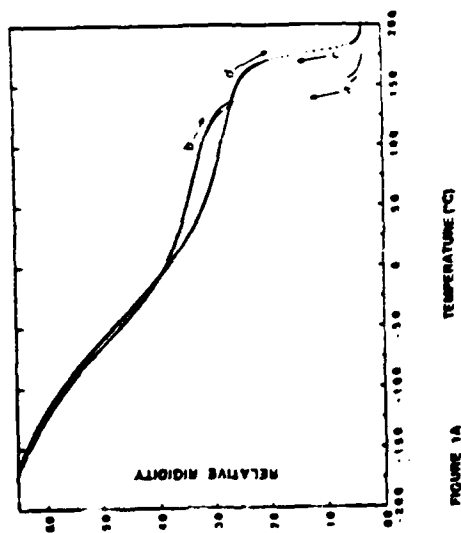
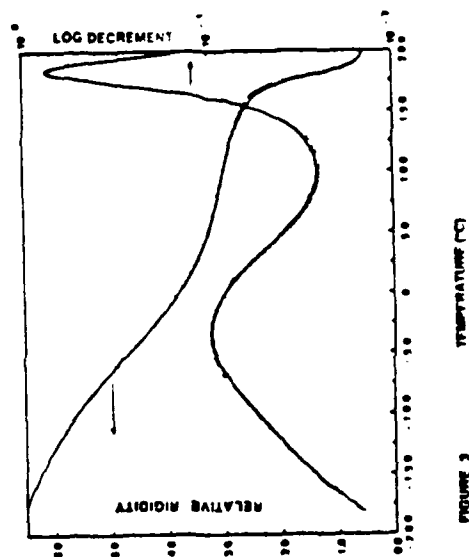
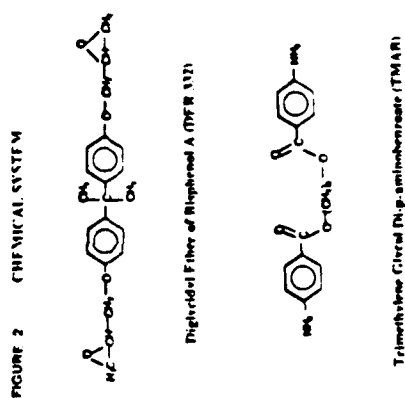
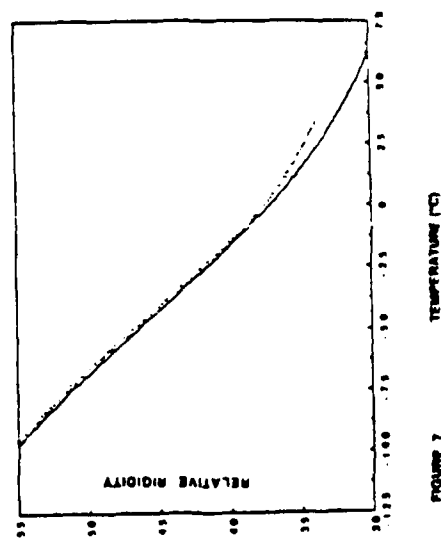
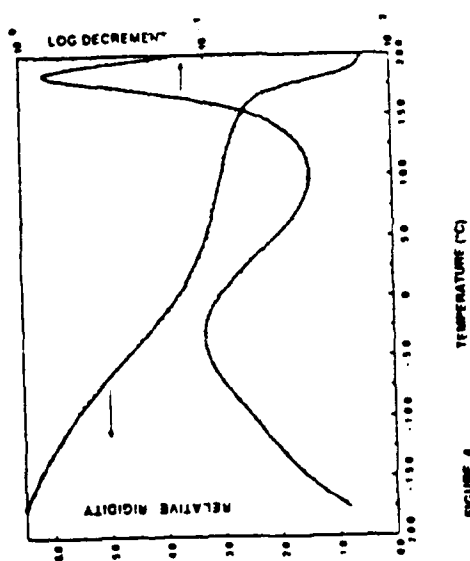
Fig. 4: Dynamic mechanical spectra (from 200 to -180°C at 1°C/min) after cure and after annealing showing the reversibility of the physical annealing phenomenon.

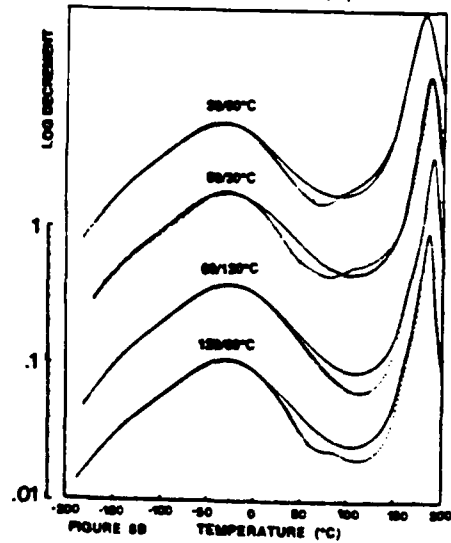
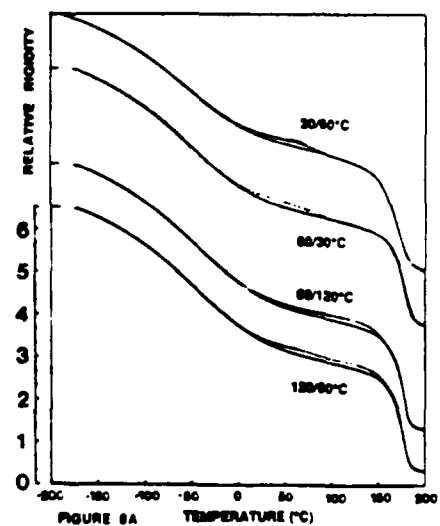
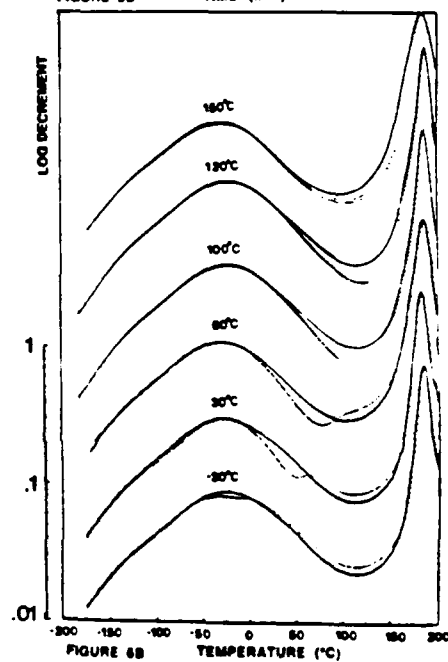
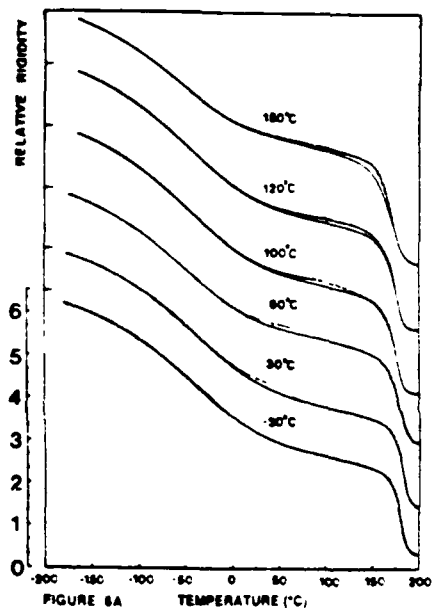
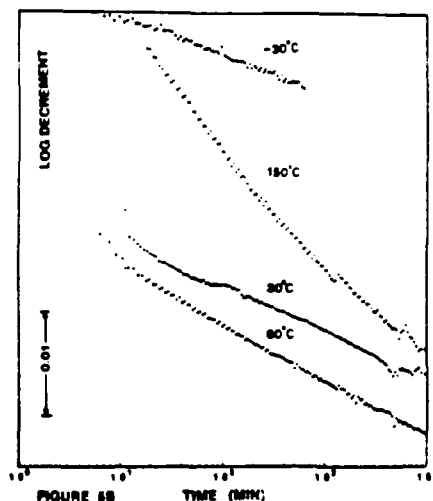
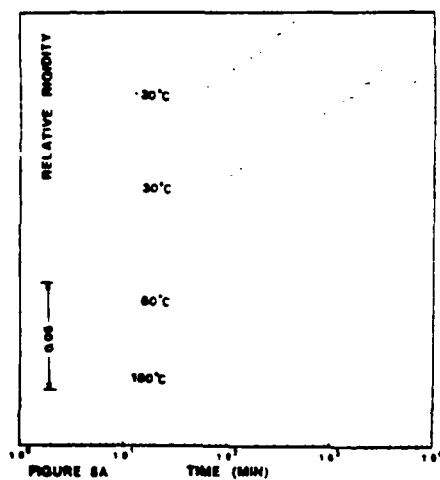
Fig. 5: A) The relative rigidity and B) the logarithmic decrement vs. time during isothermal annealing for different annealing temperatures. (Note that the vertical scale is expanded more than 100x from Fig. 6).

Fig. 6: Effects of physical annealing at different temperatures on the thermomechanical spectra of the material: (A) relative rigidity and (B) logarithmic decrement. (See text.)

Fig. 7: Expanded scale of the relative rigidity below 0°C of the specimen annealed at 30°C compared with that of the unannealed state. (See Fig. 6)

Fig. 8: Effects of the sequential annealing at two sub- T_g annealing temperatures on the thermomechanical spectra of the material: (A) relative rigidity and (B) log decrement during the temperature sequence: $T_{a2} \rightarrow -180 \rightarrow 200^\circ\text{C}$ (dotted lines) and $200 \rightarrow -180^\circ\text{C}$ (solid lines). The two numbers (T_{a1}/T_{a2}) next to each spectrum are the two annealing temperatures in the order of the annealing experiment (10,000 minutes at each temperature). The scan rates from T_{a1} to T_{a2} are 5°C/min.





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